Estimates of Atmospheric Deposition to the Mississippi River Watershed

Scott P. Dinnel
Center for Marine Science
University of Southern Mississippi
Stennis Space Center, Mississippi 39529

Abstract

Annual values of atmospheric deposition of nitrogen to the Mississippi River System drainage basin were computed for 15 years (1979– 1993) using National Atmospheric Deposition Program wet deposition data and 3 years (1990– 1992) of National Dry Deposition Network dry deposition data. Wet deposition of nitrogen was measured as nitrate (NO_3) and ammonium (NH_4), dry deposition was determined as nitrate, the sum of gaseous nitric acid (HNO_3) and particulate nitrate. Fifteen year average wet deposition of nitrate and ammonium were 44 and 42 × 109 mol/yr, respectively. Three year average dry deposition of nitrate was 33 × 09 mol/yr, approximately 75 percent the like year wet deposition of nitrate. Total annual nitrogen deposition was estimated using NADP data and literature factors for nitrite and organic nitrogen. Average atmospheric deposition of total nitrogen was estimated as 200 × 109 mol/yr. Annual atmospheric deposition of total nitrogen was compared to total Mississippi River nitrogen for the same time period. U.S. Geological Survey water quality data and U.S. Corps of Engineer water discharge data from the Mississippi and Atchafalaya Rivers were used to estimate the annual riverine flux of nitrogen. Average annual riverine nitrogen flux was determined to be 115 × 109 mol/yr. Average atmospheric deposition of total nitrogen accounts for approximately 174 percent the average total riverine nitrogen flux.

Introduction

The Mississippi River has a vast watershed; including the upper Mississippi, the Missouri and the Ohio Rivers, it drains 41 percent of the continental U.S. (Figure 94). The Mississippi River also transports high nutrient loadings from the watershed to the northern Gulf of Mexico. These nutrient loads from the Mississippi River have changed over the last four decades. There has been a doubling in nitrate, from a low in the mid-1960's to a high in the mid-1980's (Dinnel and Bratkovich, 1993), creating an enrichment of the coastal waters of the Gulf of Mexico, and contributing to the summer depletion of dissolved oxygen in the bottom waters (Turner et al., 1987). In order to manage the riverine nitrogen, an understanding of the nitrogen types and sources must be made. One useful method would be to account for all the nitrogen in the Mississippi River watershed. By quantifying the various inputs and outputs of nitrogen, a budget or mass balance, and the relative importance of each nitrogen source can be made. The input and output sources of nitrogen, especially in the vast and diverse watershed, is complex. Using the budget terms following Jaworski et al. (1992), one can appreciate the task. Input terms for a watershed nitrogen budget would be, but not limited to, waste water effluent, animal waste, soil fertilizers, atmospheric deposition, biological fixation and adsorption, importation as commodities and also in ground water. These inputs would have to balance the outputs and whatever storage that would take place. These outputs would be crop harvest, river discharge, volatilization, export as commodities and into the ground water, and denitrification. Storage of nitrogen would take place in the soil, ground water and in the biomass.

A budget such as this has been accomplished for numerous smaller watersheds, but not for one of the scope of the Mississippi River watershed. Some of these nitrogen budget terms are readably quantifiable. One is the nitrogen contained in the river discharge, an assumed major output term, it is of primary importance to the problem of the nitrogen enrichment of the northern Gulf of Mexico coastal waters. Using sampled riverine nitrogen concentrations and water discharge, one can estimate the annual flux from the watershed.

Of the suggested inputs, soil fertilizer has been cited as the leading source of nitrogen in the river discharge (Turner and Rabalais, 1991). It is conceivable that other input terms are quantifiable, and could also contribute to the nitrogen river discharge. Specifically the waste water effluent, the animal waste and the atmospheric deposition terms. It is important to determine if these terms, if any, are of sufficient magnitude as to contribute to the budget. The remaining terms are arguably more difficult to estimate. A direct comparison of any input term to a major output term would be one technique, albeit simple, in determining the relative importance of that input.

The atmospheric deposition term is one that is quantifiable, but for which no quantity has been made. Using sampled precipitation volumes and nitrogen concentrations of the precipitation, combined with estimates of non-precipitation atmospheric deposition, the annual atmospheric deposition term can be determined and compared to the magnitude of the river discharge term.

Methods

Annual Mississippi River nitrogen flux was determined as a combination of the flux down the Atchafalaya River, the major distributary of the Mississippi River, and the Mississippi River proper. Riverine nitrogen flux included total nitrate, nitrite, ammonium and organic fluxes. Riverine nitrogen flux was determined from U.S. Department of Interior (1978–1993) National Stream Quality Accounting Network (NASQAN) concentrations at St. Francisville, Louisiana and Melville, Louisiana and U.S. Army (1978– 1993) Corps of Engineers (USACOE) water discharge from Tarbert Landing, Mississippi and Simmesport, Louisiana, for the Mississippi and Atchafalaya Rivers, respectively (Figure 94). The lower Mississippi River distributes a portion of the water discharge down the Atchafalaya River. Since 1978 this annual portion has been controlled by the USACOE at 30 percent of the total discharge.

The total atmospheric deposition of nitrogen to the Mississippi River watershed was determined as the sum of wet and dry deposition of the various forms of nitrogen. These were inorganic forms such as nitrate, nitrite, and ammonium, and organic nitrogen. Wet deposition was by way of any form of precipitation, and dry deposition was by way of gaseous and particle deposition. In order to estimate annual total deposition of nitrogen various data and relationships were used.

Wet deposition of nitrate and ammonium have been sampled since 1979 by the National Atmospheric Deposition Program (NADP, 1995), sponsored by the U.S. Department of Agriculture and the U.S. Geological Survey. These are weekly concentrations and precipitation volumes for over 200 sites currently in the network. Annual mass of wet deposition of nitrogen as nitrate and ammonium were determined by summing weekly products of precipitation volume and concentrations over each year from 1979 through 1993, for each NADP site. These annual values were contoured using PLOT88, a software library of PLOTWORKS, Inc., on a 10 × 10 grid. The gridded data was then summed over the Mississippi River watershed to get the annual mass deposited by each nitrogen form. Annual wet deposition of nitrite was not measured and so was estimated as 3 percent the nitrate deposition using conservative literature relationships (Meybeck, 1982).

Information on the dry deposition of nitrogen was limited. Although the National Dry Deposition Network (NDDN) sponsored by the Environmental Protection Agency (EPA) was begun in 1986, and combined into the Clean Air Status and Trends Network (CASTNet) in 1990, the data coverage was sparse compared to the NADP data. These sites did not represent the Mississippi River watershed adequately, being predominantly located in the eastern U.S. Three years, 1990–1992, of annual NDDN dry nitrate deposition (ESE, 1995), was determined using a similar procedure as in the determination of the annual wet nitrate deposition. These watershed annual dry nitrate deposition estimates were compared to the same three years of wet nitrate deposition values. The NDDN determined dry nitrate and ammonium deposition by particulate counts of nitrate and ammonium and by sampled nitric acid gaseous concentrations combined with modeled deposition velocities. Mississippi River watershed dry nitrate deposition was estimated as 0.75 the wet nitrate deposition, an average of 1990–1992 comparisons. This was somewhat near the middle of the various dry to wet nitrate relationships reported in the literature (Table 15). Dry to wet ammonium relationships also were quite varied and poorly represent the Mississippi River watershed (Table 15). Dry ammonium was estimated as 0.25 that of wet ammonium using the average of the literature values in Table 15. Dry nitrite deposition was estimated as equal to the wet nitrite deposition. This assumption was likely to underestimate dry nitrite deposition when compared to data from the northeast U.S. where dry nitrite deposition was high (Barrie and Sirois, 1986). The total inorganic atmospheric deposition of nitrogen was estimated as the sum of measured wet nitrate and ammonium values that were increased to include estimates of wet and dry nitrite, and dry nitrate and ammonium. Wet and dry organic deposition was combined and estimated as a 1:2 organic to inorganic ratio (Hendry et al., 1981; Correll and Ford, 1982, Meybeck, 1983; Jaworski et al., 1992).

Using the stated relationships between wet and dry nitrogen forms and among different forms one could compute a total atmospheric deposition on nitrogen for the Mississippi River watershed. The relationships were all based upon the measured wet nitrate and ammonium depositions. Given the annual NADP wet depositions of nitrate and ammonium, the total wet deposition of inorganic nitrogen was the moles of ammonium plus 1.03 nitrate (0.03 as wet nitrite). Dry deposition of inorganic nitrogen was determined as 0.78 the wet nitrate (0.75 as dry nitrate, 0.03 as dry nitrite) plus 0.25 the wet ammonium. The total inorganic nitrogen was then 1.81 the wet nitrate plus 1.25 the wet ammonium. To include in an estimate of organic deposition a factor of 1.5 the inorganic nitrogen was used.

Results

The average annual total riverine nitrogen flux was 115 × 109 mol (Table 16). Total annual riverine nitrogen flux varied from <70 × 109 mol to >150 × 109 mol during the study period (Figure 95). The average major components to riverine nitrogen flux were nitrate (59 percent) and organic nitrogen (37 percent); ammonium (3 percent) and nitrite (1 percent) were minor components. Annual nitrate and organic nitrogen fluxes were fairly well correlated, with higher nitrate to organic nitrogen ratios in low discharge years.

Using a 29.3 percent average runoff or precipitation retention factor for the continental U.S. (U.S. Department of the Interior, 1984), the gauged annual Mississippi River discharge was of the same magnitude and varied in a reasonable fashion as the total annual runoff from the watershed precipitation. This supported the computational technique used here to sum parameters over the watershed, and thus in determining the total annual nitrogen deposition to the watershed as wet deposition. Spatial distribution of annual precipitation varied from a southeastern U.S. high to a Rocky Mountain low, which is in good agreement with 30 year means of the National Weather Service.

Average annual NADP atmospheric wet depositions of nitrate and ammonium were almost equal, with 44 and 42 × 109 mol, respectively (Table 16). Interannual variation was small, values were within ±10 × 109 mol of the means (Figure 96).

The annual distribution of NADP atmospheric deposition rates of nitrate (Figure 97) and ammonium (Figure 98) for 1988, a low precipitation year and 1993, a high precipitation year show a similar pattern. Highest wet deposition rates of nitrate were centered around the southern Great Lakes and extended into New England; deposition rates were lower towards the western portion of the watershed. Although nitrate wet deposition magnitude was consistent, during years of higher precipitation, the total deposition was greater and the region of highest deposition extended farther into the Midwest. Highest wet deposition rates of ammonium were also centered near the southern Great Lakes and decreased towards both coasts. During years of high precipitation ammonium magnitudes substantially increased and high deposition regions were centered in the middle of the watershed.

The NDDN dry nitrate deposition had lower annual values, but with a similar spatial distribution as the NADP wet deposition (Figure 99). The NDDN dry deposition was determined from fewer station locations and for only three years of data. The sparse spatial coverage, relative to the NADP coverage, was likely to contribute to some uncertainty in annual NDDN deposition distribution, but the magnitudes of the three years of NDDN dry nitrate deposition were considered reasonable. The three computed annual values of NDDN dry nitrate deposition were approximately 75 percent the corresponding annual values of NADP wet nitrate deposition. The limited number of years of NDDN coverage forced the use of this factor to relate annual dry nitrate deposition to the longer series of annual NADP wet nitrate deposition.

The average annual total atmospheric deposition, the sum of all measured and estimated components, was 200 × 109 mol (Table 16). This was 174 percent the average annual total riverine nitrogen flux.

Total atmospheric deposition does not exhibit the same interannual variation as the total riverine flux (Figure 100). Although both values did decrease during years of low precipitation, the magnitude of the atmospheric deposition of nitrogen was less variable.

Conclusions

It is clear that the annual total atmospheric deposition of nitrogen to the Mississippi River watershed is of the same order of magnitude, if not larger, as the annual total riverine flux of nitrogen. In a watershed nitrogen budget, one of the previously unquantified input terms, the atmospheric deposition, is found to be of comparable magnitude to one of the presumed major output terms, the riverine nutrient flux. It is therefore essential that the atmospheric deposition of nitrogen be included into any nitrogen budget of the Mississippi River watershed.

Although purposely simple, this analysis does have uncertainties in the annual nitrogen deposition quantities. The vast spatial scale of the watershed creates a number of accuracy problems. The Mississippi River watershed is composed of a number of smaller watersheds, each having different precipitation, different spatial deposition of nitrogen forms, and different depositional relationships between nitrogen forms. Wet and dry temporal variations, as well as spatial deposition variations, were optimistically accounted for with the use of annual quantities in this study.

There are still many points to clarify. First is the question of quantifying the deposition quantities of the various nitrogen forms and the modes of deposition. In this study nitrite and organic nitrogen, as well as dry nitrate and ammonium, were related to the wet deposition of two nitrogen forms, nitrate and ammonium. A number of assumed relationships were used in this study for lack of direct measurements. Additional analysis of existing dry nitrate and ammonium measurements are in order to more accurately determine the dry to wet nitrate relationship or to replace them altogether with information derived from dry deposition measurements. More information is necessary for accurate determination of both wet and dry organic nitrogen deposition. This includes both spatial watershed and multi-year temporal differences. Where decade length measurements are not available, clarification of relationships between wet to dry and between nitrogen forms are necessary.

A major component in determining the role of atmospherically deposited nitrogen is a retention factor. Even a spatial averaged retention factor, such as the continental U.S. value used in the comparison of annual precipitation volumes to river discharge, would enhance our understanding of the relative importance of the atmospheric input of nitrogen.

Certainly a more in-depth accounting is necessary in both time and space. A temporal analysis of the sub-basin watersheds using atmospheric deposition information would improve our understanding of the relationships between the atmospherically derived nitrogen and the transport by the rivers.

Remembering that the ultimate goal is the comprehensive nitrogen budget of the Mississippi River watershed, only with this level of understanding can reasonable management plans be created to address the problem of the excess riverine flux of nutrients to the northern Gulf of Mexico.

Acknowledgments

This work was the result of research sponsored by the NOAA Nutrient Enhanced Coastal Ocean Productivity program, Department of Commerce, under grant [NA90AA-D-SG688 (R/ER-20)], the University of Southern Mississippi and The Mississippi–Alabama Sea Grant Consortium.

References

Baker, L.A., 1991. Regional estimates of atmospheric dry deposition. In: Acidic deposition and aquatic esosystems. Charles, D.F. and S. Christie (eds.), Springer-Verlag, New York. p. 645–652.

Barrie, L.A. and A. Sirois, 1986. Wet and dry deposition of sulfates and nitrates in eastern Canada, 1979–1982. Water, Air, and Soil Pollution, 30:303–310.

Correll, D.L. and D. Ford, 1982. Comparison of precipitation and land runoff sources of estuarine nitrogen. Estuarine, Coastal and Shelf Science, 15:45–56.

Dinnel, S.P. and A. Bratkovich, 1993. Water discharge, nitrate concentration and nitrate flux in the lower Mississippi River. Journal of Marine Systems, 4:315–326.

Environmental Science & Engineering, Inc., 1995. CASTNet National dry Deposition Network 1990–1992 status report. Gainesville, FL. EPA-600/R-95/086.

Hendry, C.D., P.L. Brezonik, and E.S. Edgerton, 1981. Atmospheric deposition of nitrogen and phosphorus in Florida, Chapter 11, p. 199–215. In: Eisenreich, S.J., (ed.) Atmospheric Pollutants in Natural Waters. Ann Arbor Press, Ann Arbor, MI. p512.

Jaworski, N.A., P.M., Groffman, A.A Keller, and J.C. Prager, 1992. A watershed nitrogen and phosphorus balance: the upper Potomac River Basin. Estuaries 15:83–95

Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. American Journal of Science 282:401–450.

Meybeck, M., 1983. Atmospheric inputs and river transport of dissolved substances. In: Dissolved loads of rivers and surface water quantity/quality relationships. Proceedings of the hamburg Symposium, August 1983. IAHS Publ. 141. p173–192.

Shepard, J.P., M.J. Mitchell, T.L. Scott, Y.M. Zhang, and D.J. Raynall, 1989. Measurements of wet and dry deposition in a northern hardwood forest. Water, Air, and Soil Pollution, 48:225–238.

National Atmospheric Deposition Program (NRSP-3)/National Trends Network (NADP/NTN), 1995. NADP/NTN Coordination Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO 80523.

Turner, R.E., R. Kaswadji, N.N. Rabalais, and D.F. Boesch, 1987. Long-term changes in the Mississippi River water quality and its relationship to hypoxic continental shelf waters. In: Estuarine and coastal management—Tools of the trade, Proceedings of the 10th National Conference of the Coastal Society, 12–15 October, 1986, New Orleans, LA.

Turner, R.E. and N.N Rabalais, 1991. Changes in

Mississippi River water quality this century. Bioscience, 41(3):140–147.

U.S. Army, 1979–1993. Stages and Discharges of the Mississippi River and tributaries. Corps of Engineers, New Orleans District. New Orleans, LA.

U.S. Department of the Interior, 1979–1993. Surface water Quality Reports, U.S. Geological Survey. Washington D.C.

U.S. Department of the Interior, 1984. National Water Summary, 1983: Hydraulic Events and Issues. U.S. Geological Survey, Water Supply Paper 2250. Washington D.C.

Young, J.R., E.C. Ellis, and G.M. Hidy, 1988. Deposition of air-borne acidifiers in the western environment. Journal of Environmental Quality, 17(1):1–26.

Table 15.
Dry to wet deposition relationships for nitrate (NO_3) and ammonium (NH_4).

DRY:WET	LOCATION	REFERENCE
NO_3		
0.25	eastern Canada	Barrie and Sirois (1986)
0.3	midwest U.S.	Baker (1991)
0.4	northeast U.S.	Baker (1991)
0.96	Florida	Baker (1991)
1	no. New York	Shepard et al. (1989)
1	western U.S.	Young et al. (1988)
1.5	so. Blue Ridge	Baker (1991)
1.6	Tennessee	Shepard et al. (1989)
4	Florida	Hendry et al. (1981)
NH_4		
0.14	no. New York	Shepard et al. (1989)
0.19	midwest U.S.	Baker (1991)
0.25	Tennessee	Shepard et al. (1989)
0.34	northeast U.S.	Baker (1991)
0.39	Florida	Baker (1991)
0.38	so. Blue Ridge	Baker (1991)
0.5	Florida	Hendry et al. (1981)

Table 16.

Average annual Mississippi River nitrogen flux, as riverine total, nitrate (NO_3), organic nitrogen (N_{OR}), ammonium (NH_4), and nitrite (NO_2); total average atmospheric deposition of nitrogen to the Mississippi River watershed, and as nitrate (NO_3) and ammonium (NH_4); and the equivalent deposition rates for the Mississippi River watershed, 1979–1993.

NITROGEN FLUX	MEAN ($x10^9$ mol)	DEPOSITION RATE (mol/m^2)
TOTAL RIVER	115	0.036
NO_3	68	0.021
N_{OR}	42	0.013
NH_4	3.2	0.001
NO_2	1.6	0.0005
TOTAL ATMOSPHERIC	200	0.062
NO_3	44	0.014
NH_4	42	0.013

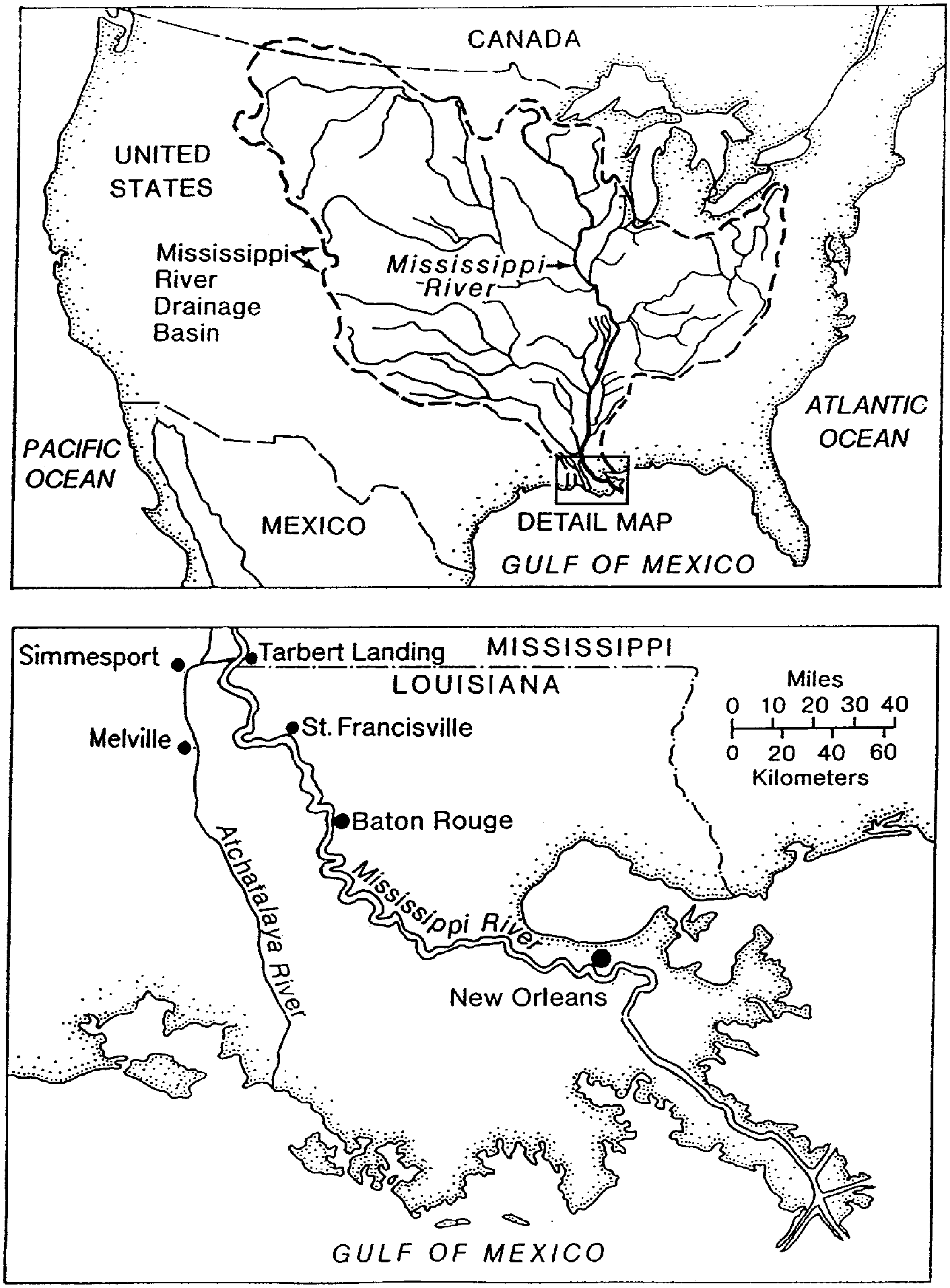


Figure 94.

General limit of the Mississippi River watershed (top). Lower Mississippi River with Atchafalaya River, USACOE discharge gauging sites at Tarbert Landing, MS and Simmesport LA, and USGS NASQAN sampling sites at St. Francisville, LA and Melville, LA (bottom). Redrawn from Dinnel and Bratkovich (1993).

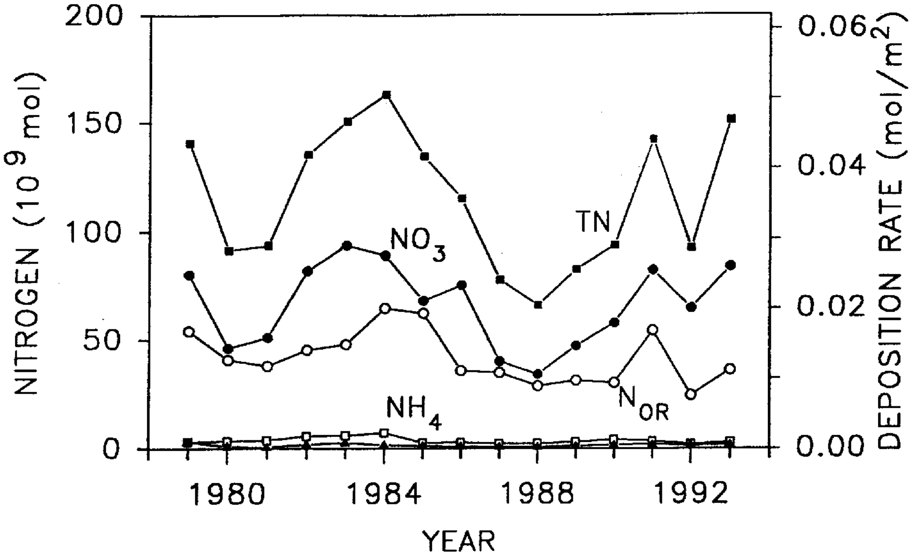


Figure 95.

Annual total Mississippi River nitrogen flux, with equivalent average deposition rate to Mississippi River watershed, 1979–1993. Total nitrogen (TN solid square), nitrate (NO_3 solid circle), organic nitrogen (Nor open circle), ammonium (NH_4 open square), and nitrite (solid triangle).

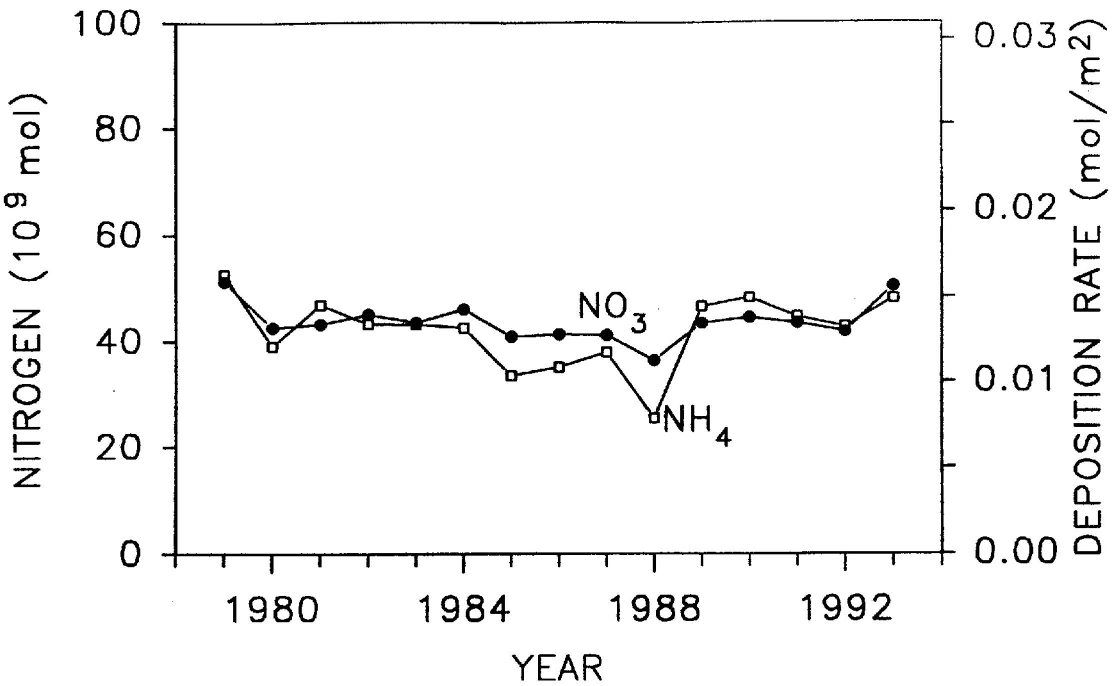


Figure 96.

Annual atmospheric wet deposition of NADP nitrate (NO_3 solid circle) and ammonium (NH_4 open square), with equivalent average deposition rate to Mississippi River watershed, 1979–1993.

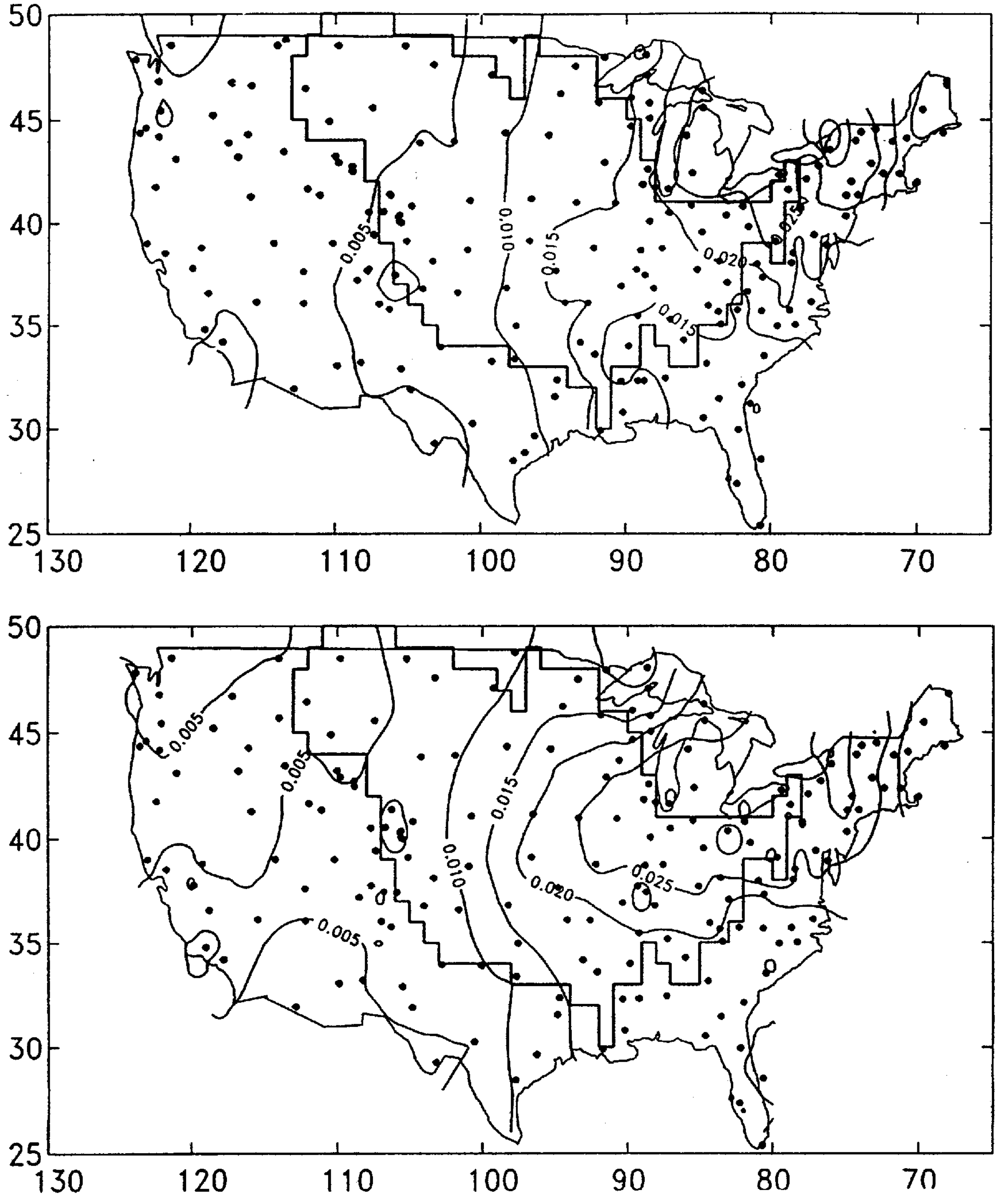
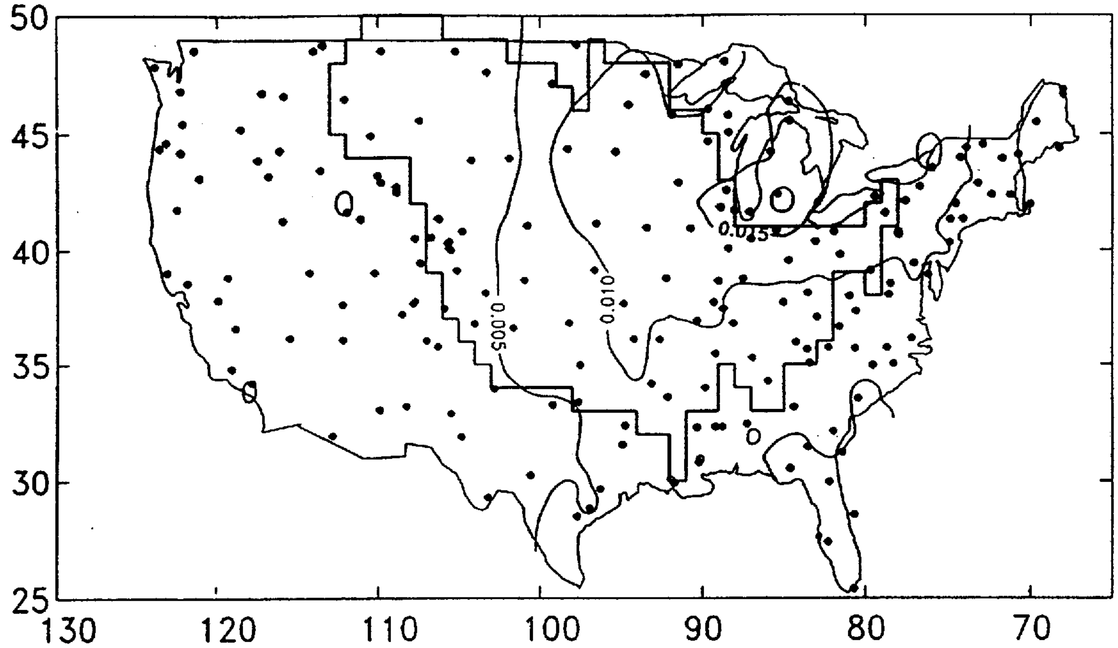


Figure 97.

Atmospheric wet deposition rate of NADP nitrate (NO_3) in 1988 (top) and 1993 (bottom) in mol/m2. NADP sites are located as solid circles; Mississippi River watershed outlined by heavy line.



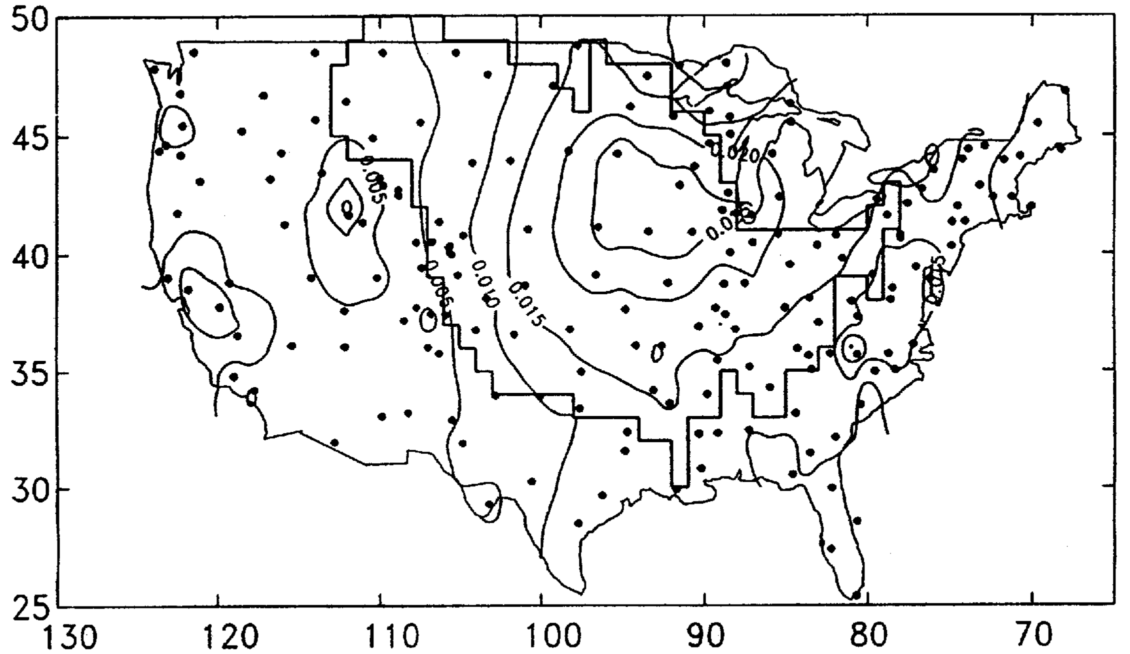


Figure 98.

Atmospheric wet deposition rate of NADP ammonium (NH_4) in 1988 (top) and 1993

(bottom) in mol/m^2. NADP sites are located as solid circles; Mississippi River watershed outlined by heavy line.

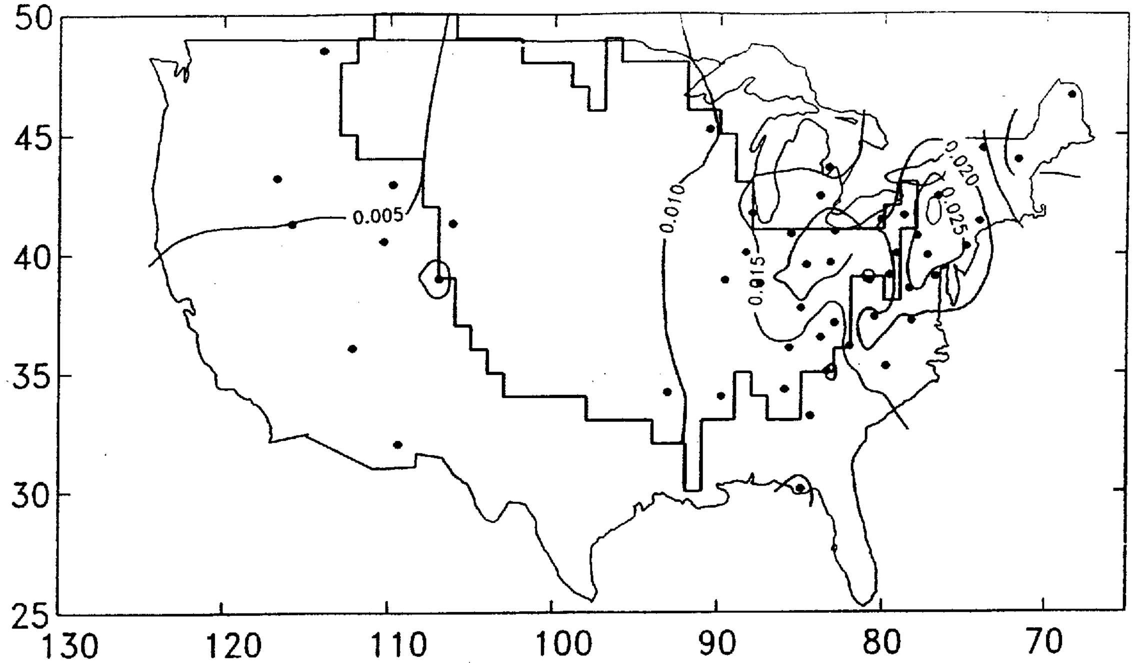


Figure 99.
Atmospheric dry deposition rate of NDDN nitrate (NO_3) in 1991 in mol/m^2. NDDN sites are located as solid circles; Mississippi River watershed outlined by heavy line.

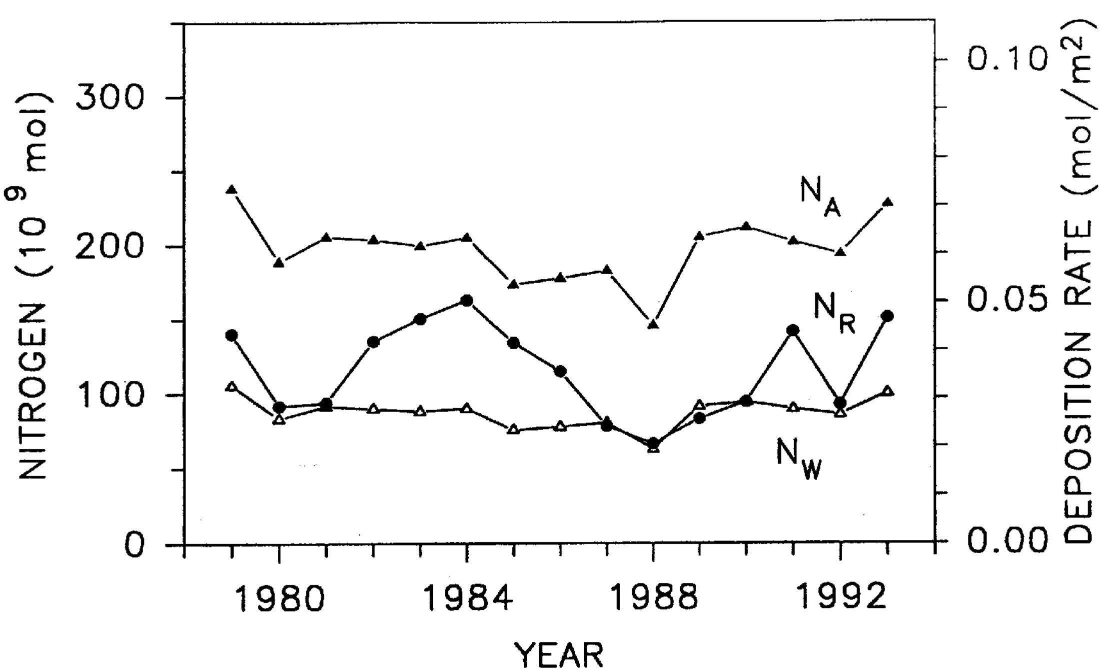


Figure 100.
Annual atmospheric deposition of total nitrogen (NA solid triangle), annual atmospheric wet deposition of nitrogen as nitrate plus ammonium (NW open triangle) and annual total Mississippi River nitrogen flux (NR solid circle), with equivalent average deposition rates to Mississippi River watershed, 1979–1993.

Presentation Discussion

Scott Dinnell (*University of Southern Mississippi—Center for Marine Sciences*)

Don Boesch *(University of Maryland— Cambridge, MD):* asked Scott Dinnell if he could quantify the export of atmospheric deposition from the landscape (groundwater) because a lot of the deposition is taking place in the northeastern part of the Basin, which tends to have higher forest cover than the rest of the Basin. This would presume to be more retentive of that source. He asked him if he has calculated some hypothetical estimates of exports.

Scott Dinnell responded that he has not quantified retention based on different landscapes in sub-basins, even between the Ohio River to the upper Missouri River, or in the plain states where land cover and soil types would cause some kind of variation of the quantities atmospherically deposited versus the amounts found in the river. He said that this type of study was another step that could be conducted. He would like to look at the spatial and temporal differences, for at least the wet deposition information.This weekly data collected over 15 years could be used to look at phasing between the deposition, the heavy deposition times, and the local river signals in the drainage basins. He felt it was important to at least look at the major drainage basins from that point of view. There is a relationship among spatial and temporal distribution and the amounts and locations of atmospheric deposition and different retention factors.